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RESEARCH RELATED TO MEASUREMENTS OF ATOMIC SPECIES IN THE EARTH'S UPPER ATMOSPHERE

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A. Introduction and Objective

Quantitative analysis by rocket- and satellite-borne mass spectrometers of the atomic oxygen density in the earth's upper atmosphere is made difficult by the reactive character of the oxygen atoms. These species can interact with solid surfaces by adsorption, by formation of oxides, and by catalytic production of molecular oxygen. Hence, the oxygen atom concentration as seen by a mass spectrometer may be substantially different from its real value in the environment because of atom removal on the surfaces of the instrument. The objective of this project is to elucidate the kinetics and mechanisms of interaction of oxygen atoms with solid surfaces of engineering interest under conditions similar to those encountered in the upper atmosphere. Such information will contribute to the quantitative interpretation of atomic oxygen composition data reported by mass spectrometers in flight.

Our experimental approach employs a reaction vessel in which the total gas pressure and the entering flux of oxygen atoms are held constant. The rate of interaction of oxygen atoms with a metal surface is evaluated by observing the diminution in atom flux at the outlet of the vessel when a specimen of the material of interest is inserted into the reactor. Our preceding reports have described and discussed the kinetics of interaction of oxygen atoms with a number of metal surfaces which have been employed in the fabrication of flight mass spectrometers. These metals included gold, silver, titanium, and stainless steel. Recently we have studied the interaction of oxygen atoms with aluminum and have commenced an investigation of the interaction of hydrogen atoms with gold.

B. Experiments

1. Oxygen Atom Measurements on an Aluminum Specimen

Reports of a number of investigators[1,2] that aluminum possesses a very low catalytic activity for oxygen atom recombination led us to examine the atom loss characteristics of this metal. We cut a specimen from 0.001-inch thick, commercial foil, obtained from the Aluminum

Corporation of America. The specimen was a narrow ribbon with a geometric surface area of 23 cm^2. Procedures described in an earlier report[3] were employed to mount the specimen in the reactor, to calibrate the mass spectrometer, and to determine the atom removal rate. Consequently, atom loss efficiency for aluminum may be compared directly with that for other metals we have investigated[4] in terms of the relative flux of oxygen atoms surviving transit through the reactor.

Before exposure to oxygen atoms, the specimen was heated in vacuum to remove adsorbed contaminants. Aluminum melts at 660°C; hence the cleaning operation had to be carried out at a very modest temperature. We maintained the specimen at 250°C for about 30 minutes; during this time water vapor was the main contaminant that desorbed from the surface.

Following this treatment of the specimen, oxygen was admitted to the system and the tungsten source was heated to 2000°C to generate oxygen atoms. The composition of the reactor effluent was monitored as a function of oxygen pressure at the inlet to the atom source region, and of temperature of the tungsten source. The observed efflux of atomic oxygen was identical to that observed in complementary experiments with no specimen in the reactor, within the limits of experimental error.

After the aluminum specimen had been exposed to gaseous oxygen atoms for more than one hour at room temperature, it was heated to 250°C for several minutes. This procedure caused no pressure pulse in the reactor that could be attributed to the desorption of oxygen or any other gas.

The aluminum specimen employed in our experiments had been stored and manipulated in air before insertion into our vacuum system. Consequently, the surface was undoubtedly covered with a layer of aluminum oxide of undetermined thickness. This oxide is extremely stable, and could not be expected to dissociate or vaporize in the high vacuum environment during the mild (250°C) cleaning treatment that we used. We conclude that the inert character of this surface toward oxygen atoms must be attributed to aluminum oxide. The lack of recombination activity

observed in our experiments is quite consistent with the reported[2] low values of oxygen atom recombination efficiency for aluminum oxide determined in higher pressure experiments.

2. Hydrogen Atom Measurements on a Gold Specimen

The desire to evaluate quantitatively the upper atmosphere particle density of hydrogen atoms from amu-1 peak amplitudes reported by the OGO-F satellite mass spectrometer, led us to an investigation of the interaction of hydrogen atoms with gold. Molecular hydrogen can be thermally dissociated; in fact, the dissociation process on a heated tungsten ribbon has been studied.[5] We chose, therefore, to employ the identical atom source used for oxygen in our experiments as a source for hydrogen atoms.

Our apparatus[3] was modified only by addition of a hydrogen inlet line and valve, in parallel with the existing oxygen inlet line. Experiments were then carried out in a manner analogous to those using oxygen; that is, the hydrogen inlet valve was opened to establish a steady state flow through the apparatus while the tungsten ribbon was heated to 1900°C, and the composition of the reactor effluent was monitored with the mass spectrometer. Specifically, we observed the ratio of atomic to molecular hydrogen (amu 1/amu 2) as a function of the pressure of hydrogen in the atom source inlet.

As might have been expected, we observed initially a mass flux of water (amu 18) in the reactor effluent as large as, or larger than, that of molecular hydrogen. The magnitude of this component diminished with time, presumably as the oxides that had accumulated in the atom source region were reduced by the atomic hydrogen. However, water remained a principal constituent in the effluent even after prolonged heating of a new tungsten ribbon in hydrogen at any temperature sufficient to dissociate hydrogen over our range of accessible hydrogen pressures.

The presence of water was undesirable because it contributed substantially to the amu-1 peak due to cracking in the ion source of

our mass spectrometer. The cracking pattern of water was determined over a range of pressures and of ionizing electron energies, but the contribution of amu-18 to amu-1 could never be reduced below 3%. This amount represented a sizeable correction to apply to observed amu-1 amplitudes in all the experiments carried out in our apparatus.

The surviving flux of hydrogen atoms, even with no specimen in the reactor, was quite small. The data show, however, that the magnitude of the surviving atom flux is significantly diminished when the gold specimen is situated in the reactor. This specimen is the identical piece of 0.002-inch foil, with a geometric surface area of 24.5 cm^2, employed in our earlier measurements with atomic oxygen.[3] The observed fractional change in surviving flux of hydrogen atoms, Q_H/Q_H^*, has a value of 0.62 (the asterisk represents the quantity associated with the empty reactor).

We also determined the rate of sorption of hydrogen atoms on the gold specimen at room temperature, using the same technique previously employed[3] to measure the rate of sorption of oxygen atoms on various metals. Under the conditions of our experiments, the rate of sorption of molecular hydrogen was negligibly small. Atomic hydrogen, however, sorbed at a finite rate which diminished with time, as shown in Fig. 1. Based on this observed change in sorption rate, we computed the sticking coefficient, S, for hydrogen atoms on gold as a function of surface coverage (Fig. 2).

C. Discussion

There is ample evidence from experiments carried out at higher pressures (up to 1 atmosphere) that gaseous hydrogen atoms will adsorb and react on a gold surface.[2,6,7] It had been tacitly assumed by most observers that, upon exposure to atomic hydrogen, a gold surface would be rapidly populated to unit coverage, because the adsorption of such gaseous atoms is a nonactivated process. However, our present data (Fig. 1) indicate that hydrogen atoms reach a limiting coverage on gold equivalent to less than 0.1 monolayer (1 monolayer $\sim 10^{15}$ atoms/cm^2). As yet, we have no direct experimental evidence relating the steady

state limit of coverage to the pressure of atomic hydrogen. It is of interest to note, however, that the hydrogen atom recombination efficiency of a gold specimen at 25°C was determined in our earlier work[2] to have a value of 0.072 when exposed to atomic hydrogen at a pressure of approximately 10^{-3} torr. The close agreement of this value with the clean surface sticking coefficient of 0.06 (Fig. 2), considered together with the low steady state degree of coverage, tempts us to suggest that hydrogen atom recombination occurs on a gold surface by a Langmuir-Hinshelwood mechanism (reaction between adjacent sorbed atoms) at a rate that is limited by the adsorption process. If this be the case, chemisorbed hydrogen is very weakly bound on gold and exists in a highly mobile state. A few additional experiments at different partial pressures of gaseous atomic hydrogen are required to clarify this situation. Such measurements, in addition to direct determinations of the rate of associative desorption of chemisorbed hydrogen from gold, are being pursued.

The rather small effect of the gold specimen on the flux of hydrogen atoms surviving transit through the reactor ($Q_H/Q_H^* = 0.62$) is not inconsistent with the adsorption rate results, if we assume that no atom recombination occurs by way of an Eley-Rideal mechanism (reaction between a gas atom and an adatom). Such an assumption is quite reasonable in view of the low steady state adatom coverage observed in our experiments (Fig. 1).

D. Practical Conclusions

The highly inert and stable character of aluminum oxide-clad aluminum toward oxygen atoms indicates that this material might be quite acceptable as a material of construction for flight mass spectrometers. One note of caution should be raised. There is some evidence, from earlier experiments carried out in our laboratory, that the aluminum oxide surface coating on an aluminum wire can be slowly reduced by prolonged exposure to atomic hydrogen. The hydrogen atom density in the upper atmosphere is very low; yet, over long periods of time such a surface change might occur, with consequent, unpredictable effect on the rate and nature of oxygen atom interaction.

The hydrogen atom-gold interaction picture is not yet complete. The results so far indicate that the rate of loss of hydrogen atoms on gold is relatively low, so that corrections to be applied to amu-1 data reported by the OGO-F flight mass spectrometer would be small. One might anticipate that an oxygen-saturated gold surface exposed to an incident flux of hydrogen atoms would consume the reactants by the catalytic production of water. Indeed, Harteck and Reeves reported[8] that the rate of loss of oxygen atoms on gold increased when atomic hydrogen was present. Nevertheless, the rate of this reaction has not been evaluated quantitatively. The fact that an amu-1 peak is being reported by the gold-plated OGO-F mass spectrometer from an ambient environment where hydrogen atoms are a very minor constituent relative to oxygen atoms suggests that under such conditions the hydrogen-oxygen reaction on gold is not particularly efficient.

E. Future Work

Our immediate plans are: (1) to complete our investigation of the interaction of hydrogen atoms with gold; (2) to assess, if possible, the effect of presorbed oxygen on the atomic hydrogen interaction on gold; (3) to construct and carry out selected experiments in a reactor of more squat geometry that will be amenable to precise theoretical treatment.

F. Personnel

Personnel who have participated in this program during the past quarter include Bill R. Baker, Henry Wise, and Bernard J. Wood.

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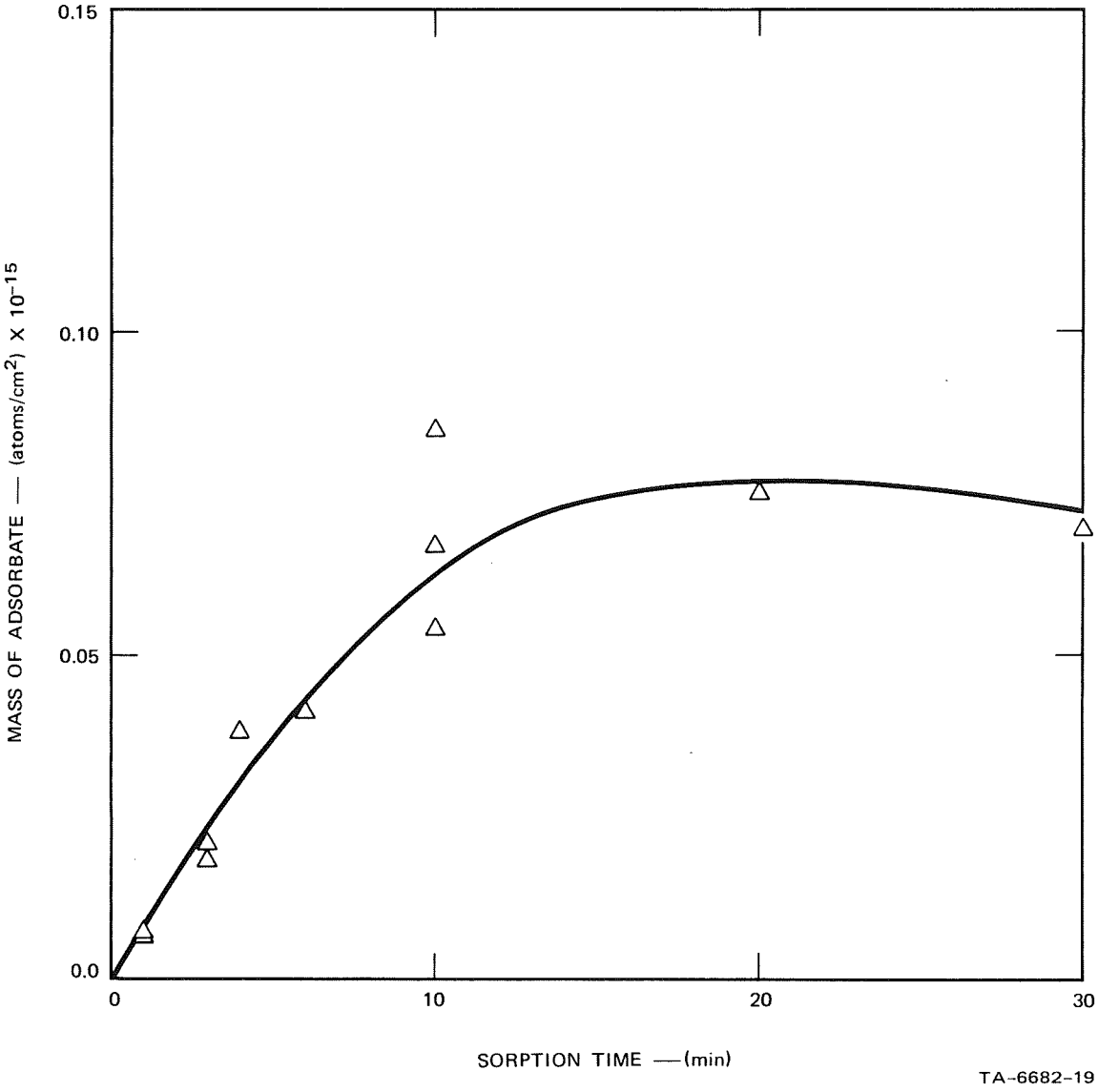

FIGURE 1 MASS OF HYDROGEN ATOMS ADSORBED ON A GOLD SURFACE AT 25°C AS A FUNCTION OF EXPOSURE TIME. Time 0 indicates cessation of heating of gold specimen to 650°C. $P_H \approx 1 \times 10^{-9}$ torr; $P_{H_2} \approx 2 \times 10^{-7}$ torr.

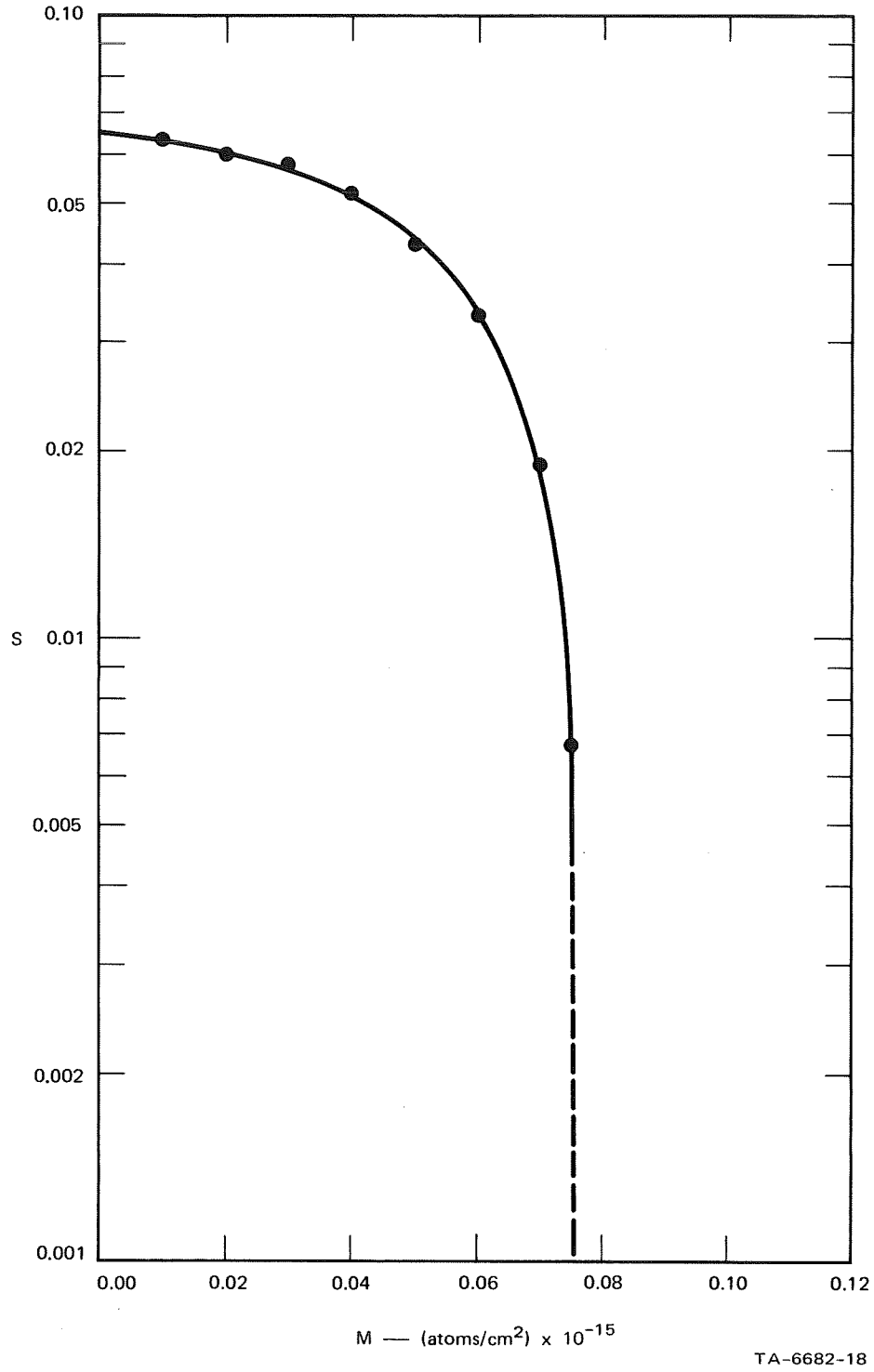

FIGURE 2 STICKING COEFFICIENT, S, OF HYDROGEN ATOMS ON A GOLD SURFACE AT 25°C AS A FUNCTION OF SURFACE COVERAGE, M. $P_H \approx 1 \times 10^{-9}$ torr; $P_{H_2} \approx 2 \times 10^{-7}$ torr.